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OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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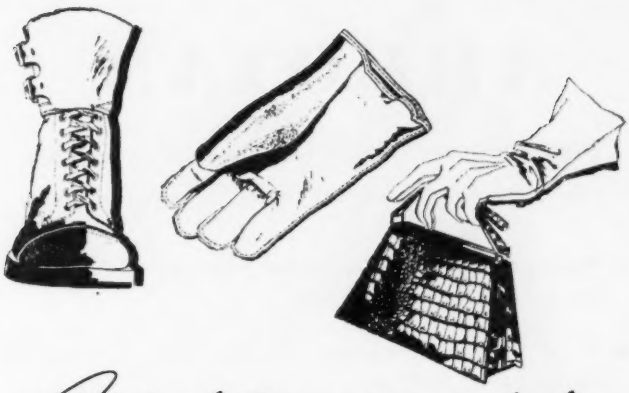

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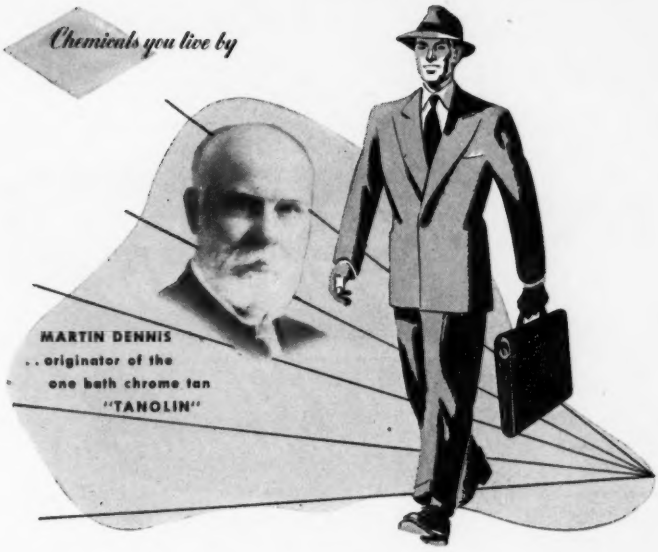

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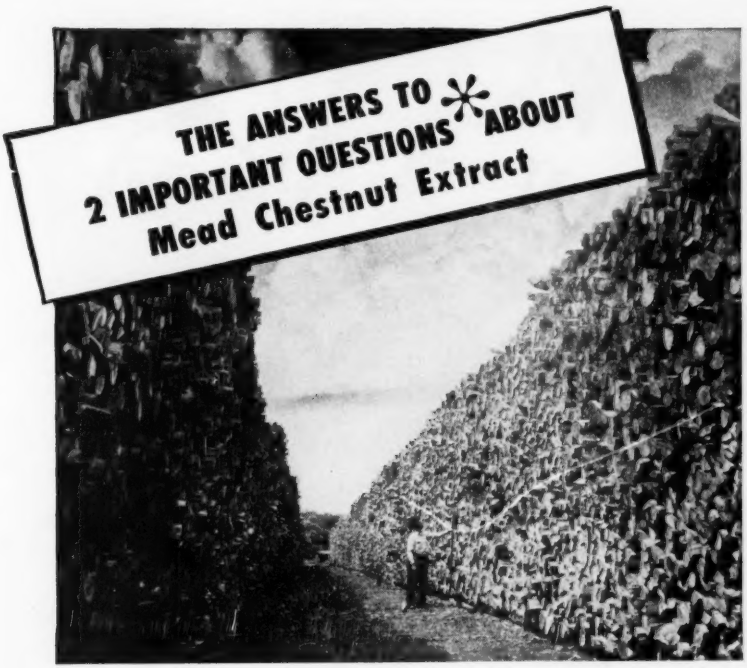

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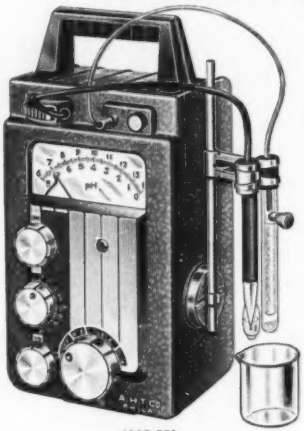

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VOL. XLVI DECEMBER 1951 No. 12

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The Isolation of Hydroxyproline and Proline from Collagen II*

By JOHN H. HOWARD

Department of Basic Science in Tanning Research
University of Cincinnati,
Cincinnati 21, Ohio

We have recently reported a new method [1] for isolating hydroxyproline and proline from collagen. The method involves treating a collagen hydrolyzate with 0.3 N nitrous acid in the presence of 1 N hydrochloric acid at 60°C for 1.5 hours followed by refluxing for one hour; solvent, sodium chloride, and residual hydrogen chloride removal; finally extracting with absolute ethanol to obtain white, crystalline proline and hydroxyproline in crude form. The yields of the crude proline and hydroxyproline were 15 to 50 per cent of the theoretical values (as reported by Neuman [2] and Neuman and Logan [3]). On analysis, the products were found to be about 50 per cent pure. For the process to be of commercial value, pure hydroxyproline and proline must be obtained. This paper deals with the various techniques which we employed in trying to reach this goal.

METHODS

1. *Anion Exchange Resin*

Synthetic resins are reputed to be effective agents for anion and cation removal. Large volumes of liquid must be employed and concentration (especially of solutions containing biological materials) must be carried out in vacuo. Even with these complicating factors, it was deemed advisable to attempt a larger scale experiment with use of an anion exchange resin to remove residual hydrogen chloride in order to improve the yields of proline and hydroxyproline both in quality and quantity, the theory being that these amino acids, being such weak acids, would not be retained on the column, but would pass on through, and only the hydrogen chloride and possibly the deaminates of the rest of the amino acids remain behind.

A 50 gram charge of collagen was hydrolyzed and decolorized. Then the material was nitrated, concentrated, extracted with concentrated hydrochloric acid, the last extracts combined, taken to dryness in vacuo, decolorized, and finally passed through an Amberlite IR$_4$ column in the manner prescribed by the manufacturer of the resin [4]. The column was regenerated with ammonium hydroxide whenever the pH of the effluent fell below 4.0. The column was regenerated from time to time because the iso-electric point of proline [5] is at pH 6.3 and that of hydroxyproline [5] is at 5.82 and a solution having a pH of less than 5.82 would therefore contain acidic materials other

*This work was supported by the Office of Naval Research.

than proline and hydroxyproline. None of the cuts were without a trace of color as they emerged from the column although the affluent was water-white. The combined effluents when concentrated to 150 ml. by vacuum distillation, were orange-brown in color. This could not be removed completely with two treatments of Norit-A. Further solvent removal in vacuo yielded a mahogany colored gunk, devoid of crystals. Absolute ethanol extraction of this material and further treatment of the ethanol extracts (by taking to a syrup in vacuo, taking up in water, decolorizing, taking to a syrup again in vacuo, and extracting with absolute ethanol) yielded four crops of crystalline materials. Their analyses are given in Table I. The first crystal crop weighed 1.14 grams. It was white and slightly hygroscopic. The second crystal crop weighed 0.28 g. It was light brown in color and hygroscopic. The third crystal crop weighed 0.09 gram. It was light pink in color and was slightly hygroscopic. The fourth crystal crop weighed 0.06 gram. It was brown in color and was very hygroscopic.

None of the above fractions are pure. Organic material is still present as evidenced by the inability to make a material balance. The ash content of each fraction is still quite significant. Qualitative tests again indicated the ash in all cases to be essentially phosphates. The Norit-A was probably the main contributor of this component since it was found to contain 2.24 per cent ash on an as is basis and this ash was essentially phosphates.

Inability to make a nitrogen balance is every case indicates that either racemization of the proline has occurred (the microbiological assay reports only the natural isomer) or the Amberlite IR$_4$ contributed nitrogen to the products and this last is quite logical since the resin is an aniline-formaldehyde condensation product. It would further appear that the resin either removed most of the proline, or the nitrogen containing compound contributed by the same catalyzed the degradation of the proline, as a result of which no true proline fraction was recovered. We must therefore conclude that the entire foregoing method offers no improvement over that as originally developed by us [1].

II. Minimum Treatment with Norit-A

This was a large scale experiment employing 50 grams of collagen. The entire process was carried out in the manner already described [1] except that the material was not decolorized until just after treatment with hydrogen sulfide for the removal of residual silver ions, the purpose being to minimize the contribution of the carbon to the final products. Another innovation was the use of hydrogen chloride prior to initial sodium chloride removal, again to get rid of as many inorganic materials as possible.

The hydroxyproline fraction weighed 2.02 grams. It was a white powder and was slightly hygroscopic. Its analysis is given in Table I. No crystalline proline fraction could be obtained! This was, undoubtedly, due to the fact

that the pH of the mixture could not be elevated beyond 3.0 during the silver carbonate treatment for residual hydrogen chloride removal, due to organic acids, resulting from the deamination of the other alpha amino acids, thus preventing proline separation as a crystalline entity. The low yield and purity of the hydroxyproline fraction along with failure to obtain crystalline, crude proline force us to conclude that this technique is no improvement over the original method [1] and the point where decolorization is carried out is quite critical.

Using the picrate method, as outlined by Hamilton and Ortiz [6], on a portion of the material remaining after initial hydroxyproline removal was of no value to the solution of the problem. White crystalline material was obtained but it was mostly ash and contained less than one per cent total nitrogen.

III. Six Normal Hydrochloric Acid for Nitrosamines' Hydrolysis and for Hydroxy Acid Removal.

This was a large scale experiment using 50 grams of collagen. The method was the same as Method II in this paper except that, after nitrating, concentrated hydrochloric acid was added so that the normality of the solution was six with respect to that acid. The rest of the procedure was standard. Analysis of the solution after hydrolysis of the nitrosamines showed 80.7 per cent of the theoretical amount of hydroxyproline to be present. By analogy, the same amount of proline persisted. The 20 per cent loss of hydroxyproline and proline was undoubtedly due to volatilization of their nitrosamines during hydrolysis of the same. Had the material been confined to an all-glass, reflux set-up instead of simmering in an open flask, all of the proline and hydroxyproline would still have been present. Analysis of the silver salts, which were by-products of the procedure, showed them to contain no nitrogen indicating that no loss of proline or hydroxyproline took place during the silver carbonate and hydrogen sulfide treatments.

As with Method II, no crystalline, crude proline was obtained. However, the yield of crude hydroxyproline was the highest so far obtained. It weighed 4.60 grams, was snow white, and was only minutely hygroscopic. Its analysis is given in Table I.

Again, failure to obtain proline in crystalline form was probably due to the organic acids still present since silver carbonate was ineffective in elevating the pH of the solution above 3.0 during residual hydrogen chloride removal. As in Method II, the picrate procedure was outlined by Hamilton and Oritz [6] was of no value in obtaining more proline and hydroxyproline after initial removal of the latter.

We can therefore conclude that Method III is the most superior one so far developed by us for obtaining hydroxyproline in the great quantity and purity. Failure to obtain crystalline, crude proline shows again what will work in small quantities often requires more study when applied to larger batches.

TABLE I

Analyses* of Various Crystalline Fractions
Isolated from Collagen with Use of Nitrous Acid

Method	Fraction	Ash	Chlorides	Ammonia Nitrogen	Total Nitrogen Found	Total Nitrogen Calculated**	l(−)Proline	Hydroxyrpoline
I	Crop No. 1	12.7	0.0	0.00	6.35	5.09	9.7	36.6
I	Crop No. 2	18.3	0.0	0.00	6.02	5.33	7.9	40.9
I	Crop No. 3	11.5	0.0	0.00	8.78	8.81	19.0	60.9
I	Crop No. 4	28.1	0.0	0.00	5.41	2.97	15.1	10.6
II	Crop No. 1	18.8	——	——	6.09	——	——	29.0
III	Crop No. 1	5.5	——	——	9.36	——	——	63.2
IV	Hydroxyproline	3.6	——	——	10.21	8.77	6.5	74.7
IV	Proline	0.0	——	——	9.13	——	——	24.3
IV	Hydroxyproline II	14.2	——	——	5.06	——	——	17.6
V	Hydroxyproline	42.0	——	——	3.93	4.11	2.4	35.8
	Proline	0.0	——	——	9.63	9.50	5.0	83.3

* In grams per hundred grams of material dried 16 hours at 60°C in vacuo.
**Calculated from the per cent nitrogen in the per cents proline and hydroxyrpoline as found by analysis.

IV. Recycling with 6 N Hydrochloric Acid to Facilitate Removal of Organic Impurities.

One gram of the crude hydroxyproline from Method III was recycled as per that method starting with boiling with 6 *N* hydrochloric acid (but not including nitrating) and using three 400 ml. aliquots of 6 *N* hydrochloric acid. The rest of the process was standard. Two white, crystalline fractions were finally obtained. The hydroxyproline fraction weighed 0.46 gram and was non-hygroscopic. The proline fraction weighed 0.01 gram and was very hygroscopic. The analyses of these two fractions are given in Table I. Only a few analyses were carried out on the proline fraction due to insufficient material. The inability to make a nitrogen balance, in the case of the hydroxyproline fraction, is probably due to the total nitrogen value being in error as witness the results of the nitrogen balances for the materials obtained using Method V.

The above hydroxyproline is the purest so far obtained and the yields are good. The method is therefore of value as an adjunct to Method III for improving the purity of the crude hydroxyproline.

All of the material from Method III, remaining after the initial hydroxyproline removal, was recycled in a similar manner. No crystalline proline was obtained but a second crop of hydroxyproline was isolated. Its analysis is given in Table I, coded hydroxyproline II. It weighed 0.08 gram, was white, and was slightly hygroscopic. The low yield and purity of the hydroxyproline fraction along with failure again to obtain proline in crystalline form indicate that recycling of the gunk, after initial hydroxyproline removal, is of little value.

V. Refluxing with Absolute Ethanol to Improve Hydroxyproline Purity.

A portion (0.2 gram) of the hydroxyproline from Method IV was refluxed for 18 hours with 200 ml. of absolute ethanol. Two crystalline fractions were obtained. The hydroxyproline fraction was white and non-hygroscopic, and weighed 0.01 gram. The proline fraction (the absolute ethanol soluble fraction) was orange in color and non-hygroscopic and weighed 0.04 gram. The analyses of these fractions are given in Table I. The treatment caused just the reverse of the expected! The hydroxyproline fraction is low both in quantity and quality. The proline fraction turns out to be the purest hydroxyproline so far obtained! However, the yields are low and we are not of the opinion that this method is of positive value to the solution of our problem.

Discussion

None of the foregoing methods gives pure proline and hydroxyproline. In fact, hyroxyproline may be considered to be the only product. The particular anion exchange resin used is of no value to the solution of our problem. Other resins may show promise, but we did not have the time to investigate them. As in a great many cases, what works for small quantities, does not work on a larger scale. The presence of large quantities of hydroxy acids inhibited proline separation in the larger scale experiments. Both proline hydrochloride and hydroxyproline hydrochloride are soluble in absolute ethanol to a large extent. The hydroxy acids, after hydrogen chloride removal, would thus account for the presence of proline in the hydroxyproline fractions and vice versa. The hydroxy acids are also soluble in absolute ethanol which accounts for their high concentration in the proline fraction and their inhibiting action.

The use of 6 *N* hydrochloric acid for nitrosamines' hydrolysis is of value and is now our standard procedure. Recycling the crude hydroxyproline by boiling with 6 *N* hydrochloric acid gives purer hydroxyproline but does not appear to offer possibilities for complete hydroxy acid removal as carried out. However, vacuum-steam distillation using 6 *N* hydrochloric acid may be the answer to our problem. It appears from the nitrogen balances, that racemization of neither proline nor hydroxyproline has taken place during process using Methods III, IV, and V.

Summary

1. We have presented five methods for improving the quantity and quality of hydroxyproline and proline isolated from collagen with use of nitrous acid.
2. Amberlite IR_4 offers little value toward improving our original method.
3. When 6 *N* hydrochloric acid is used for nitrosamines' hydrolysis, at least 80 per cent of the theoretical hydroxyproline and proline are still present as their hydrochlorides. We therefore change our original method to include this feature.

4. The silver salts, which are by-products of the process, do not cause any loss of nitrogenous material.
5. Recycling of crude hydroxyproline by boiling with 6 *N* hydrochloric acid improves the purity of the compound.
6. Recycling of the gunk, remaining after initial hydroxyproline removal, by boiling with 6 *N* hydrochloric acid is of no value to the process.
7. The use of picric acid for additional proline and hydroxyproline separation, after initial removal of the latter, is of no value.
8. Refluxing crude hydroxyproline with absolute ethanol fails to improve the process.

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Aluminum Acetate in the Development of Alum Retannage*

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We have previously reported [1,2,3,4] that alum retannage imparts to vegetable-tanned leathers resistance to deterioration such as that caused by acids (which may be absorbed from acid-polluted atmospheres), moist heat, or molds. These reports show some of the chemical and physical changes which occur in vegetable-tanned leather when treated by this process. The amount of combined tannin is increased, with a corresponding decrease in the amount of soluble tannin. There is an increase in the degree of tannage. There is

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a rise in the shrinkage temperature to more than 100°C. Tensile strength, stretch, and water vapor permeability are only slightly affected by the retannage. Porosity is increased, and water absorption is somewhat decreased. Like leather tanned by other types of mineral tannage, alum-retanned leather is difficult to "wet back" after it has been completely dried. (These changes are shown by the data from one of these reports [1], given in Table I.) These properties suggested that alum retannage might be advantageously used to overcome insole failures, which are a serious problem in Army shoes. Preliminary track and actual wear tests indicated that replacement of vegetable-tanned leather insoles by alum-retanned leather insoles would materially reduce the number of failures.

TABLE I

Effect of Alum Retannage on Vegetable-Tanned Leather

	Vegetable-Tanned Leather	Alum-Retanned Leather
Al_2O_3, per cent	——	2.8
Soluble tannin, per cent	12.2	7.5
Combined tannin, per cent	35.2	39.9
Degree of tannage, per cent	76	90
Shrinkage temperature, degrees cent.	87	112
Tensile strength, lbs./sq. inch	1900	2020
Relative porosity	151	334
Relative water vapor permeability	0.5	0.6
Stretch at breaking point, per cent	22	30
Water absorption, per cent	52	44

The method of retannage, as previously reported, called for a comparatively weak liquor consisting of an aqueous solution of aluminum sulfate made to a basicity of 25° Schorlemmer and containing one mole of sodium acetate for each mole of Al_2O_3 as a "masking" or stabilizing agent. Tanning with this liquor in tanning vats or drums required several days. Later work has been directed toward developing a more rapid process, which could be easily and effectively applied in a commercial tannery to supply sufficient leather for a wear test on a fairly large scale.

With this objective, attempts were made to develop a "dry-dip" method. In this method, the dry leather is dipped into an alum solution of the proper strength and temperature. When the leather has absorbed a sufficient amount of the solution, it is removed, sammied and dried. During sammying and drying, the absorbed Al_2O_3 combines with the leather. The dip solution used was a solution of aluminum sulfate made to 25° basicity with sodium carbonate and containing sodium acetate. In these preliminary dry-dipping tests, penetration was poor, combination of Al_2O_3 with the leather was incomplete, and the mineral content of the leather was high. Apparently the dry-dipping

process was unsatisfactory when aluminum sulfate and sodium acetate solutions were used.

Another method studied was the incorporation of the aluminum salts in the conventional tanner's oil wheel with the oil and other ingredients commonly added to the leather in this manner. Table II shows results of several pilot-scale tests of this method.

TABLE II

Pilot-Scale Oil Wheel Retannage Tests with Aluminum Sulfate*

Test Number		1	2	3	4
Aluminum sulfate $Al_2(SO_4)_3 18H_2O$, used,	pounds	16.0	24.0	32.0	55.0
Sodium acetate $NaAc.3H_2O$ used,	pounds	3.2	4.8	6.4	11.0
Alkali used,	pounds	2.6**	4.0**	6.7**	9.1†
Borax used,	pounds	1.2	1.8	2.4	4
Epsom salts added,	pounds	5.3	5.3	5.3	7
Other materials added††	pounds	8.2	8.2	8.2	7
Total ash in leather,	per cent	11.2	15.9	17.5	17.9
Combined Al_2O_3 in leather,	per cent	1.8	2.8	3.2	4.9
Shrinkage temperature of leather,	°C.	92–95	98–105	105–107	102–108
pH of leather,		3.59	3.90	4.01	3.87

*Retanning materials were dissolved to a concentrated solution before they were added to the oil wheel. Twenty-five bellies, equivalent to approximately 125 lbs. of dry leather, were used in each test.

**Sodium hydroxide.

†Sodium carbonate.

††This includes all materials normally added in the oil wheel except oil and epsom salts. The leathers received the regular oil mix.

For each of these tests, 25 bellies, totaling approximately 125 pounds dry weight, were used. The amounts of aluminum sulfate, sodium acetate, and borax used were varied as shown in Table II. The wet bellies, after bleaching and wringing at the tannery, were taken to the laboratory and put in the warmed laboratory oil wheel (inside size, 30″ wide x 6′ diameter). The retanning solution, containing aluminum sulfate, sodium acetate and alkali, and the sugar and oils at 155° F., were added while the wheel was running. In Test No. 4, borax and Epsom salts were added in the tanning liquor; in the other tests, the salts and filler materials were added dry before starting the wheel. The stock was drummed for 1 hour, after which the leather was removed, allowed to sammy, and dried slowly for 8 days. The leathers from Tests 1, 2, and 3 were rough dried at the tannery, that from Test 4 was dried at the laboratory. After rough drying, all the leathers were sour-dipped, rolled, and dried at the tannery.

The results in Table II show that with increasing amounts of aluminum sulfate used there was a corresponding increase in the combined Al_2O_3 in the leather (the average values obtained from a representative number of bellies). The percentage of Al_2O_3 varied slightly from belly to belly in the same lot,

as indicated by the range in shrinkage temperatures. When finished and dried at the laboratory, the bellies had little tendency toward cracky grain. When they were finished, rolled, and dried at the tannery, however, the grain was cracky. The difference in drying technique between the laboratory and the tannery was that in the laboratory the leathers were slowly dried until they reached the proper moisture condition, whereas in the tannery they were dried beyond this point and then wet back to give the desired moisture content.

This retanning process was then applied on a tannery scale; 200 bellies were used for each of four tests. Various amounts of materials were used, as indicated in Table III. After bleaching and wringing as usual, 200 bellies were placed in the oil wheel. For tests 1 and 2, salts, filler, borax, and clay were added dry, and the wheel was run for 3 minutes; then the alum retannage solution was added, and the wheel was run for 40 minutes. Next, the oil-sugar mixture was added, and the wheel was run for 20 minutes. In Tests 3 and 4 the aluminum sulfate, sodium acetate, and borax were added separately in dry form in the order given, and the wheel was run for 15 minutes after each addition. The regular filler materials and salts were then added, and the wheel was run for 5 minutes. The liquid sugar-oil mix was next pumped into the wheel and the wheel was run for 10 minutes.

TABLE III

Plant-Scale Oil Wheel Retannage Tests with Aluminum Sulfate*

Test number		1**	2†	3†	4†
Aluminum sulfate, used,	pounds	400	100	100	150
Sodium acetate, used,	pounds	50	12	12	18
Alkali used,	pounds	65††	10‡	——	——
Borax used,	pounds	30	8	50	75
Epsom salts added	pounds	32	32	32	20
Other materials added‡‡	pounds	140	140	140	140
Total ash in leather,	per cent	20.5	10.0	11.9	13.4
Combined Al_2O_3 in leather,	per cent	5.7	1.6	2.1	2.9
Shrinkage temperature of leather,	°C.	101–108	83–85	88–89	93
pH of leather,		3.82	3.29	3.49	3.51

*Two hundred bellies, equivalent to approximately 1,000 lbs. of dry leather, were used for each test.

**All retanning materials dissolved to a conentrated solution before adding to the oil wheel.

†All materials added dry to the oil wheel.

††Sodium carbonate.

‡Sodium hydroxide.

‡‡This includes all material normally added in the oil wheel except oil and epsom salts. The leathers received the regular oil mix.

Table III shows the results of these tests. In the first test, a much higher fixation of alum was obtained than desired, because the amounts of materials used were calculated on an average 5-pound belly, whereas actually the bellies weighed far less. The bellies from this first test were quite cracky. Bellies

from Tests 2 and 3 showed practically no crackiness; those from Test 4 showed slight crackiness. These results indicated that from 2.50 to 2.75 per cent Al_2O_3 would probably be the optimum amount. Comparison of Tables II and III shows that the shrinkage temperatures in Table III were not so high as would be expected from the Al_2O_3 content. This may have been due to poor combination of the Al_2O_3 when added dry. In addition, when the materials were added dry there was a wide variation of Al_2O_3 content in bellies from the same lot, thus indicating uneven distribution.

As shown by Tables II and III, the ash content of the leathers retanned in the oil wheel was high. It was much higher than that obtained in our previous method of tannage. This may be explained by the difference in the methods used. In vat or drum retanning with a comparatively weak alum liquor, the Al_2O_3 is thoroughly combined, and is not removed by subsequent washing. The remaining mineral matter in the liquors is not combined, and is quite thoroughly removed by washing. In the oil-wheel process, however, none of the uncombined mineral matter is removed because there is no subsequent washing, and therefore it remains in the leather and increases the ash content. It was believed that this high mineral content might be one cause of crackiness; therefore it seemed advisable to obtain a retanning solution containing less mineral matter.

It seemed possible that this mixture of aluminum, sulfate, sodium, and acetate ions might be replaced by a mixture of aluminum and acetate ions, which would be given by aluminum acetate. The stabilizing acetate ion would be given directly by the salt used, and, in addition, less alkali would be required to bring the solution to the desired pH. A solution of aluminum acetate may easily be prepared, but the preparation of a powder or even a concentrated solution presents some difficulties.

An aluminum acetate solution of satisfactory purity was prepared in the laboratory by the reaction between solutions of aluminum sulfate and calcium acetate; the precipitated calcium sulfate was filtered off. Since this solution was too dilute to use by the oil-wheel method, tests were made by the dry-dip process previously found unsatisfactory for the aluminum sulfate-sodium acetate method. In preliminary laboratory tests with the aluminum acetate solutions, results were quite satisfactory. It was found that the distribution, penetration, and combination of the Al_2O_3 were good. These results indicated that a dry-dip process might be satisfactory if an aluminum acetate solution were used instead of an aluminum sulfate-sodium acetate solution.

As a quick means of determining the amount of combination and the distribution of the Al_2O_3 in the leather, we have found shrinkage temperature determinations and a simple boiling test very valuable. Although it is not necessarily true for all leathers that quality may be judged by resistance to moist heat, much information in regard to the completeness and uniformity

of retannage in the alum-retanned leathers may be obtained by these tests. If, after being exposed for 3 minutes to boiling water, the leather does not shrink or shrivel and darken in the interior it may be judged that combination and distribution of the Al_2O_3 are satisfactory.

It might not be feasible to prepare an aluminum acetate tanning solution in the tannery by the reaction between aluminum sulfate and calcium acetate. However, manufacturers of aluminum compounds have now developed a method of preparing an easily soluble basic aluminum acetate powder. Solutions of this material containing the equivalent of 3 to 5 per cent Al_2O_3 have pH values of 4.4 to 4.8, well within the optimum range for fixation of Al_2O_3 in leather. Laboratory tests indicated that this material was quite satisfactory for retannage.

Retannage tests were made with basic aluminum acetate for producing alum retanned leathers in both pilot-scale and plant-scale lots. Results of these tests have been summarized in Table IV. The first was a pilot-scale test conducted in the laboratory in which 21 bellies were used. The aluminum acetate in concentrated solution was applied uniformly to the bellies by hand; they were then put in the laboratory oil wheel and drummed with the regular tannery filler materials for 10 minutes. The regular tannery sugar-oil mixture was added to the running wheel, and the wheel was run for 55 minutes. The bellies were then removed, piled and allowed to sammy for 48 hours, after which they were returned to the tannery for drying and finishing.

TABLE IV

Oil Wheel Retannage Tests with Aluminum Acetate

		Pilot Scale (Laboratory)	Plant Scale (Tannery)	
Estimated weight of bellies	pounds	105	1,000	1,000
Aluminum acetate used	pounds	11.7*	106*	50**
Epsom salts used	pounds	3.0	0	16
Ash in leather	per cent	9.9	8.4	2.6–3.5
Al_2O_3 in leather	per cent	4.6	3.5	1.4–2.1
Shrinkage temperature	°C.	116	116	91–104
pH of leather		3.90	4.43	3.70–3.89

*Aluminum acetate added in solution.
**Aluminum acetate added dry.

The other two tests were made on a plant-scale at the tannery. In the first of these tests, 200 bleached and wrung bellies were placed in the oil wheel, the concentrated solution of aluminum acetate was poured in, and the wheel was run for 20 minutes. The regular quantity of filler, but no Epsom salts, was added, and the wheel was run for 10 minutes, after which the regular sugar-oil mix was pumped in, and the wheel was run for 30 minutes. The

leather was then slowly dried, sour-dipped, rolled, and finished. In the second test, the bellies were washed with water in a wheel, then bleached and wrung before the alum retannage was applied. The amounts of aluminum acetate and Epsom salts were 50 pounds and 16 pounds, respectively. These materials were added in dry form, and the wheel was run for 10 minutes. The usual sugar-oil mixture and clay were added, and the wheel was run for 10 minutes. No fillers were used. The bellies were slowly dried, sour-dipped, rolled, and finished.

In the pilot-scale test and the first tannery test, the aluminum acetate was dissolved before it was added. In the other test, the dry material was added, and the results show that there was considerable variation in the completeness of retannage between the individual bellies in this test. It is believed that application of aluminum acetate in dry form results in nonuniform absorption and retannage. The results obtained in these tests, however, indicate that the use of aluminum acetate instead of the aluminum sulfate-sodium acetate mixture gives a firmer combination of Al_2O_3, as the shrinkage temperatures in general are higher for a comparable amount of total Al_2O_3. The amount of mineral matter is also reduced. All these leathers, when dried slowly in the laboratory to the proper moisture content, showed little tendency toward cracky grain. When they were overdried, however, and then wet back, the grain became tender. Figure I shows the stratigraphic distribution of Al_2O_3 in the leather when this method was used.

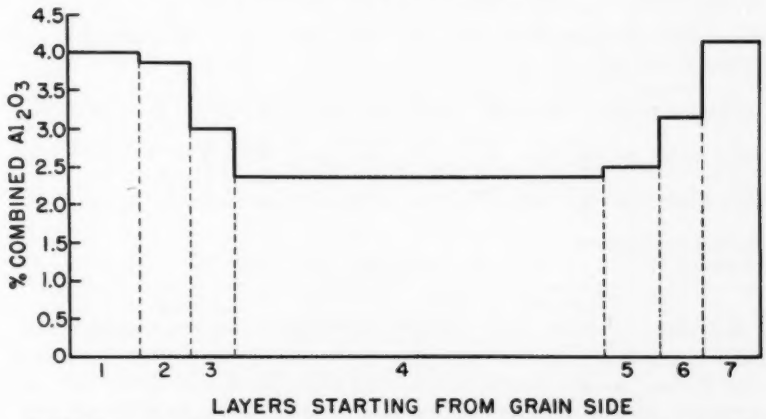

FIGURE 1. Stratigraphic Distribution of Al_2O_3 in Leather. Aluminum Acetate–Oil Wheel Method.

Commercial basic aluminum acetate was also used successfully in dry dipping tests. Table V shows some of the conditions studied, and the results obtained by dipping at 45° C., which appeared to be the optimum tempera-

ture. Concentration of solution and time of dipping were varied. The results indicated that a dipping time of ½ hour will usually be satisfactory. The concentration of the solution must be varied according to conditions. Leathers from different tannages vary in the amount of solution they will absorb in a given time, and this point must be determined by test. Furthermore, leathers of different thickness from the same tannage will have different absorption capacities, so leathers must be sorted into three or four thickness classifications before dipping. The variations in pickup of solution and Al_2O_3 shown in Table V are wide, but represent various tannages. The last five tests, which were made with leather of the same tannage, show the variations, due mostly to thickness, which might be expected. The data show that, under proper conditions, leather of the desired Al_2O_3 content, probably 2.50 to 2.75 per cent, may be made and that the Al_2O_3 in this leather will be firmly fixed and well distributed, as indicated by boiling tests and shrinkage temperature determinations.

TABLE V

Dry-Dip Retannage Tests with Aluminum Acetate at 45° C.

Test number	1	2	3	4	5	6	7	8	9	10
Concentration of solution in Al_2O_3, per cent	2.5	3.0	3.0	3.0	4.0	4.0	4.0	4.6	5.3	5.3
pH of solutions	——	4.42	——	4.47	——	——	——	4.49	——	4.55
Time of dipping, minutes	10	5	10	60	10	30	30	30	30	30
Pickup of solution on dry leather weight, per cent	66.7	63.3	84.4	58.8	101.7	36.8	50.0	51.0	54.7	57.0
Ash in leather, per cent	3.1	5.1	5.6	4.3	5.2	3.2	5.5	5.2	5.5	6.6
Al_2O_3 in leather, per cent	1.8	2.5	3.1	2.0	3.0	1.9	2.5	2.6	3.0	3.3
Shrinkage temperature of leather, °C.	100	109	115	100	124	102	110	111	116	116

A number of insoles were retanned in the laboratory for testing by the Office of the Quartermaster General of the Army. In carrying out the retannage of these insoles, several results were observed that indicated that the retannage process could be applied more advantageously to bellies or belly centers than to finished cut soles. In the first place, the finished cut soles contain a fairly large amount of loading material and have been rolled and finished to the desired degree of firmness. Retannage of finished cut soles tends to increase to an undesirable extent both the mineral matter content and the firmness of the leather. The edges of the soles became overtanned

and cracky. Insoles are cut from leather which has been rolled in a moist condition. Some of the leather fibers have been put under an unnatural tension, which is released when the leather is wet. During the wetting operations incidental to alum retannage, this tension is released, resulting in a distortion of the sole pattern. For these reasons, we have found it desirable to apply the alum retannage to rough bellies and then load and finish to the required firmness. This procedure will reduce the losses resulting from shrinkage, distortion, and edge effect to a minimum.

One objection to alum retannage is the production of tender or cracky grain. For many purposes where the grain is to be removed by light buffing, this is of little significance. We have found that crackiness may be largely eliminated by observing certain precautions. The amount of Al_2O_3 in the leather should be no higher than necessary. A desirable range appears to be 2.5 to 2.75 per cent. The amount of other mineral matter, such as Epsom salts, added to the leather should be reduced so that the total mineral matter will not be excessive. A light oiling of the leather after retannage is beneficial. Finally, the leather should not be overdried, which appraently is one cause of crackiness.

Summary

The use of basic aluminum acetate for alum retannage of vegetable-tanned insole leather was shown to be more effective than retannage with aluminum sulfate which has been stabilized and neutralized to the desired basicity. Retannage may be carried out in regular tannery oil drums, but results indicate that retannage applied in the form of a dry dip to rough whole bellies or belly centers followed by oiling and finishing is to be preferred. In applying the retannage, the tanner will find it necessary to adjust the process to his own type of leather.

For the appraisal of serviceability, leather should be produced commercially by the proposed method in quantity adequate for large-scale wear tests.

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Discussion

S. S. Kremen: Those of you who have followed the work with the improvement of insole leather know that the alum retannage is considered to be fundamentally capable of marked improvement.

The principal weakness which has to be overcome is the cracky grain or tender fiber. Certainly Mr. Beebe has indicated that the possibility is that it can be done.

I believe from talking to Mr. Rogers that there is one fundamental problem which is causing most of this trouble—a problem which is common to all attempts to retan or post-tan vegetable leather as produced in the tannery.

You have to clean the grain and bleach it in the tannery. You could just follow the bleach, but at that stage the stock is coming through quite rapidly, and it is moved to the wringer in large amounts. You cannot then, without causing quite a bit of disruption in the tannery process, leave the stock overnight in the tanning bath in the optimum way.

In this whole business you can have a great deal of trouble in any retanning with formaldehyde and chrome as well as the alum if you try to do it without assuring slow and uniform penetration and going through a thorough stripping to protect yourself from this cracky grain.

The whole problem is, that if you want some improvement in the quality of your leather, you have to be prepared to make some modifications in the process along the lines that Dr. Merrill pointed out. Yes, it is surprising when you make an improvement if you don't have to rebalance your whole process.

I think all of us who are trying to improve the quality of insole leather are meeting with that very problem—this understandable hesitancy to rebalance the whole procedure while keeping it on an economic basis so that you can do your post-tanning.

What I feel is the key to all these troubles that you run into is that there must be recognition that the whole process should be considered. It might possibly be the case that retannage may be done more conveniently at a different stage. Most of them now are done either in the oil wheel or dip.

I wonder if anybody has any idea whether perhaps you might get sufficient improvement without the undesirable properties by doing it after the rocker yard when you may have sufficient tannage, and also the time to conveniently handle the procedure.

BEEBE: I think it would be most desirable to adjust the retannage to fit a normal tanning process as nearly as possible.

KREMEN: Are there any questions or comments from the floor?

J. S. ROGERS: In our early studies of alum retannage, we did use some leather taken at earlier stages in the tanning, and that worked quite satisfactorily.

Later on we thought it desirable to consider doing this work after the bleach because we found that bleaching leather after it had been alum retanned had a tendency to remove the alum tannage from the surfaces of the leather, particularly the grain surface, and some from the flesh surface. Such leathers, when subjected to the boil test would show a certain amount of shrinkage in these areas after bleaching.

That is one of the reasons why we thought it desirable to do this work after bleaching. I think the alum retannage applied to leathers that have been partially stripped to remove excessive tanning materials from the grain area is desirable because the application of the alum retannage in the grain results, as you probably have noticed, in a fixation of any uncombined tanning materials that are there. That, naturally would have a tendency to form an area that would be likely to be brittle and have a tendency to crack.

We feel that this difficulty can be overcome. In fact, we have prepared samples in the laboratory that have been successful in this direction, and we believe further tests in the tannery will enable us to prepare a leather that will be satisfactory in that respect.

We have developed in the laboratory a testing machine which is ready for making dynamic tests on the insole leathers when we have leather that we feel will justify actual testing in this way, and also have a sufficient quantity of leather for use in actual service tests for correlation with the laboratory tests.

I think then we will be able to appraise these leathers more satisfactorily.

KREMEN: I would like to know the preferred pH range for alum retannage. Secondly, was any work done on a companion or comparatively similar process based on aluminum formate.

C. W. BEEBE: The pH range runs 3.8 to 4. In regards to the use of aluminum formate there was none commercially available.

Furthermore, we have tried sodium formate in our previous tests along with other materials, and found sodium acetate was the best stabilizing material for alum retannage. That doesn't necessarily apply to chrome retannage but does to alum.

If there is a commercial aluminum formate available we would like to try it.

The Application of Statistics in the Tanning Laboratory†

I. The Use of a Youden Square

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INTRODUCTION

When carrying out experiments in the laboratory on the processing of small pieces of hides or skins, we have been confronted with the problem of

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how to design our experiments so that we may draw valid conclusions which can be used to establish the best procedures for large scale tanning tests. For several years we have been concerned with the evaluation of various agents, both tanning and chemical, as they affect weight yield, shrinkage temperature, plumping, grain drawing and other physical and chemical characteristics. During the course of our experimentation it was observed that employment of a naphthalene syntan in conjunction with a methylol melamine resin markedly plumped chrome tanned leather in the flank areas of the hide in contrast with those close to the backbone. Measurements showed that there was a variation in the degree of plumping obtained when compared either in a direction from butt to neck or from backbone to flank. These observations indicated that the structure of the hide was playing an important role. Also, they indicated that the influence of hide structure would have to be removed for the proper evaluation of experiments carried out with small pieces of leather.

This was accomplished by laying out our sampling positions in the form of a simple 4 x 4 Latin Square [1]. Such a design allows for the comparison of four different treatments replicated four times and the removal of effects in a vertical and horizontal direction. Since it frequently happens that we wish to compare more than four treatments the use of the 4 x 4 square would necessitate the employment of a control each time a new set of variables was to be investigated. Since this design was not efficient when a comparison of a large number of treatments was being made the need for a better experimental procedure was evident.

Brownlee [1] describes various systems of analysis which possibly could be applied to this problem. Two of these, originated by Yates [2] and Youden [3], respectively, appeared promising.

Yates has proposed a series of designs consisting of incomplete blocks, that is, the treatments in each block do not constitute a complete replication. This scheme, however, did not appear desirable since the effect of position on a treatment can be eliminated in one direction only. In Youden's method the effect due to position can be eliminated in two directions since each row constitutes a complete replication, and the number of blocks is the same as the number of treatments. The Youden squares may be considered to be a portion of a Latin Square, with some rows missing. For example, 16 treatments could be arranged in a sixteen by sixteen Latin Square of a particular type. If this square were divided horizontally into two parts, one of 6 rows and one of 10 rows, then one of the designs would consist of 16 incomplete blocks with 6 treatments in a block and with each row a complete replication. It should be noted that in this design each treatment occurs twice in a block with every other treatment.

We shall show how a Youden Rectangle of this design was employed by us in an experiment in the tanning laboratory.

Glossary of Terms

An explanation of the terms used in statistical work with particular reference to this experiment is given below. A more general explanation may be found by referring to Brownlee [1], and other textbooks.

Treatment: This is defined as the one variable deliberately introduced for purposes of evaluation. In this case, the treatments are sixteen tanning formulae which we propose to study.

Block: This is a small portion of an experimental area, which is assumed to be of relatively uniform character, to which the treatments are applied. In the analysis of an experiment laid out in blocks, that portion of the variation due to blocks must be separated from that due to treatments as well as from that portion representing experimental error. In this experiment, each block represents a neck to butt strip of leather consisting of six, 6″ x 6″, squares lying in a vertical axis (see Figure 1).

Replication: This is the number of times each treatment is observed. The design used in this experiment requires six replications, i. e., each treatment was applied to six squares of leather.

Efficiency: This has been described as a measure of the loss of information which is inherent in the design [3].

Design of the Experiment

In designing our experiment we outlined sixteen tanning formulae employing naphthalene syntans, both acid and neutral, in conjunction with a methylol melamine resin with or without the addition of mineral and organic acids. These treatments were planned so that we would be able to determine the significance of the following factors as related to the plumping of the leather:

1. Overnight aging of the leathers in the treating solution.
2. Type of acidifying agent, i. e., sulfuric acid, and acid naphthalene syntan, and organic acids.
3. Prolonged washing of the leathers after the resin application.
4. Pretreatment of the leathers with neutral and acid syntans prior to resin application.
5. The application of the resin in the absence of a naphthalene syntan.

An outline of the sixteen treatments which were carried out to determine the effects of the above variables is given in Table I.

Sixteen retanning treatments were assigned a letter, A to P, and the letters arranged in the 16 x 6 rectangle [3]. Youden arranged his columns so that the top row was in alphabetical order. This sequence, however, was modified by randomizing the order of the columns. This does not affect the properties of the whole design in any way, since the vertical order of each column remains the same (see Figure 1).

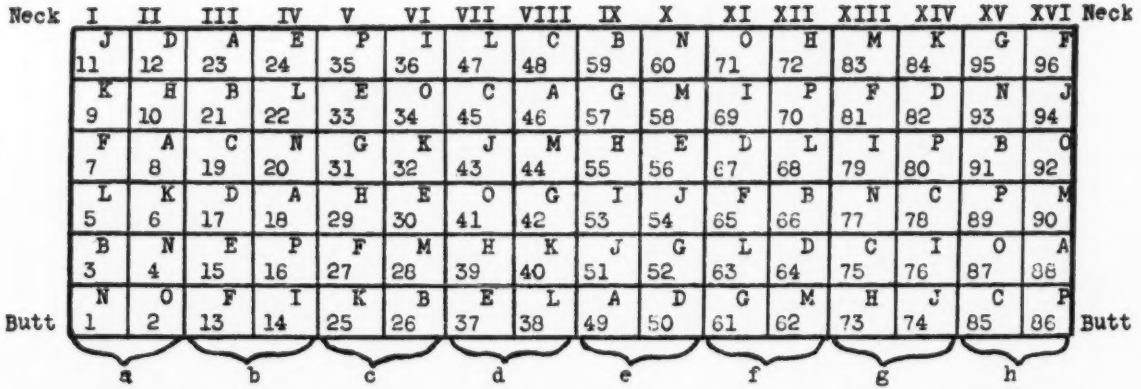

FIGURE I—16 x 6 Youden Square Showing Grouping of Treatments and Replications on Eight Sides of Chrome Stock.

I-XVI=Block Number
A-P =Treatment Number.
1-96 =Leather Number.
a-h =Side Number, a, c, e, g, =Left Sides
b, d, f, h =Right Sides

TABLE I

Tabulation of Syntan-Resin Processes Showing Assignment of Treatments

Treatment	Leather Numbers	Syntan Pretreatment	M.M.R.† Added	Drumming Time Prior to Acidification	Acidifying Agent Used	Drumming Time After Acidification	Aging Period
A	8-18-23-46-49-88	3% N.N.S.*	3%	120 min.	None	——	——
B	3-21-26-59-66-91	"	"	"	None	——	Overnight
C	19-45-48-75-78-85	"	"	90 min.	1% H_2SO_4	30 min.	——
D	12-17-50-64-67-82	"	"	"	1% H_2SO_4	30 min.	Overnight
E	15-24-30-33-37-56	"	"	"	1% H_2SO_4	30 min.	Wash 30 min.
F	7-13-27-65-81-96	3% A.N.S.**	"	120 min.	None	——	——
G	31-42-52-57-61-95	3% A.N.S.	"	90 min.	3% A.N.S.	30 min.	——
H	10-29-39-55-72-73	"	"	"	1% CH_3COOH	"	——
I	14-36-53-69-76-79	"	"	"	1% HCOOH	"	——
J	11-43-51-54-74-94	"	"	"	3% A.N.S.	"	Overnight
K	6- 9-25-32-40-84	"	"	"	1% CH_3COOH	"	Overnight
L	5-22-38-47-63-68	"	"	"	1% HCOOH	"	Overnight
M	28-44-58-62-83-90	None	None	Drummed	120 min. in water	——	——
N	1- 4-20-60-77-93	None	3%	120 min.	None	——	——
O	2-34-41-71-87-92	3% N.N.S.	None	120 min.	None	——	——
P	16-35-70-80-86-89	3% A. N.S.	None	120 min.	None	——	——

*Neutral Naphthalene Syntan
**Acid naphthalene Syntan.
†Methylol melamine resin.

Experimental

The methylol melamine resin used was a spray dried water-soluble type. A typical analysis is given below; it will be designated hereafter as "M.M.R."

Total nitrogen	36.0%
Total formaledhyde	43.4%

The neutral naphthalene syntan was a spray dried sodium salt having an active ingredient of approximately 74%. This material will be designated as "N.N.S.".

The acid naphthalene syntan was a spray dried partially neutralized product. The acidity of this syntan was equivalent to 11.0% calculated as sulfuric acid and contained approximately 51% of active ingredient. This syntan will be designated as "A.N.S.".

Eight sides of split and shaved chrome tanned leather, four left and four right sides, were wet back in a drum and horsed to drain under cover overnight. For blocks I and II, twelve pieces of leather, 6" x 6", were cut from side "a", as shown in Figure 1, and the corresponding numbers punched in the lower left corner of each piece. The right edge of Column II is adjacent to the backbone. This procedure was repeated on the remaining sides. The numbered leathers were separated into their treatment groups, weighed, and stored in a closed container in a refrigerator until ready for use.

Prior to each retannage, the leathers were withdrawn from storage and thickness measurements were taken. These measurements were made on each piece at 16 different positions with the aid of a 6" x 6" template having 16 evenly spaced holes. The thickness reading was taken approximately 10 seconds from the time the foot of the amthor thickness gauge made contact with the leather. The average thickness of each leather piece was obtained from these measurements which are recorded as 1×10^{-3} inches.

After the thickness measurements had been recorded, the leathers were washed in demineralized water for 20 to 30 minutes, drained and subjected to their respective treatments using the tanning drums described by Morash & Tremberth [4]. A set of four treatments was carried out on each of four successive days.

The methylol melamine solutions were prepared by dissolving the resin in water at 120°F. followed by cooling to 105° F. prior to adding to the drum. The liquor temperature was kept at 100°F. during drumming and at room temperature when aging overnight.

All of the leathers were washed following treatment, then wrung twice under moderate pressure and allowed to horse for at least an hour in order to affect proper moisture equilibrium. Thickness measurements were again taken at this point, and the average increase for each leather was recorded with respect to its location in the Youden Square, as illustrated in Figure 2.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	Sums of Rows
J 17.13 11	D 14.81 12	A 12.50 23	E 13.19 24	P 3.68 35	I 11.63 36	L 12.75 47	C 16.00 48	B 14.94 59	N 5.19 60	O 4.88 71	E 11.75 72	M 2.06 83	K 12.00 84	G 11.06 95	F 11.31 96	174.88
K 17.37 9	H 12.68 10	B 16.07 21	L 15.87 22	E 12.69 33	O 5.62 34	C 13.81 45	A 14.94 46	G 14.56 57	M 2.81 58	I 10.25 69	P 6.88 70	F 12.50 81	D 13.93 82	N 5.25 93	J 17.44 94	192.67
F 14.87 7	A 13.88 8	C 14.56 19	N 8.75 20	G 16.00 31	K 13.68 32	J 15.32 43	M 3.50 44	H 13.19 55	E 9.94 56	D 12.31 67	L 13.00 68	I 13.19 79	P 7.25 80	B 15.19 91	O 6.50 92	191.13
L 16.19 5	K 13.94 6	D 14.81 17	A 14.38 18	H 13.31 29	E 10.50 30	O 6.44 41	G 16.50 42	I 12.31 53	J 13.12 54	F 8.68 65	B 15.07 66	N 9.32 77	C 13.00 78	P 5.56 89	M 3.12 90	186.25
B 16.56 3	N 6.94 4	E 10.37 15	P 4.88 16	F 11.88 27	M 2.06 28	H 10.88 39	K 15.00 40	J 16.56 51	G 10.50 52	L 10.13 63	D 13.31 64	C 14.12 75	I 11.63 76	O 5.50 87	A 16.68 88	177.00
N 7.69 1	O 4.93 2	F 8.43 13	I 13.00 14	K 13.50 25	B 13.31 26	E 8.81 37	L 12.50 38	A 11.43 49	D 12.38 50	G 8.94 61	M 2.94 62	H 11.19 73	J 12.38 74	C 11.81 85	P 5.75 86	158.99
89.81	67.18	76.74	70.07	71.06	56.80	68.01	78.44	82.99	53.94	55.19	63.95	63.38	70.19	54.37	60.80	1080.92
							Sums of Blocks									Grand Total

FIGURE 2—Thickness Increases of Wet Treated Leathers Arranged in Youden Square.

TABLE II

Thickness Differences of Wet Leathers Arranged in the Form of Balanced Incomplete Blocks Showing Treatment Totals and Q Values.

Treatment	Block Number I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	Treatment Totals	Treatment Totals x6(V)	Block Sums of Treatments(VI)	QValue (V-VI)
A	—	13.88	12.50	14.38	—	—	—	14.94	11.43	—	—	—	—	—	—	16.68	83.81	502.86	436.22	66.64
B	16.56	—	16.07	—	—	13.31	—	—	14.94	—	—	15.07	—	—	15.19	—	91.14	546.84	423.66	123.18
C	—	—	14.56	—	—	—	13.81	16.00	—	—	—	—	14.12	13.00	11.81	—	83.30	499.80	410.13	89.67
D	—	14.81	14.81	—	—	—	—	—	—	12.38	12.31	13.31	—	13.93	—	—	81.55	489.30	386.19	103.11
E	—	—	10.37	13.19	12.69	10.50	8.81	—	—	9.94	—	—	—	—	—	—	65.50	393.00	396.62	-3.62
F	14.87	—	8.43	—	11.88	—	—	—	—	—	8.68	—	12.50	—	—	11.31	67.67	406.02	415.98	-9.96
G	—	—	—	—	16.00	—	—	16.50	14.56	10.50	8.94	—	—	—	11.06	—	77.56	465.36	395.99	69.37
H	—	12.68	—	—	13.31	—	10.88	—	13.19	—	—	11.75	11.19	—	—	—	73.00	438.00	414.57	23.43
I	—	—	—	13.00	—	11.63	—	—	12.31	—	10.25	—	13.19	11.63	—	—	72.01	432.06	397.62	34.44
J	17.13	—	—	—	—	—	15.32	—	16.56	13.12	—	—	—	12.38	—	17.44	91.95	551.70	425.74	125.96
K	17.37	13.94	—	—	13.50	13.68	—	15.00	—	—	—	—	—	12.00	—	—	85.49	512.94	433.48	79.46
L	16.19	—	—	15.87	—	—	12.75	12.50	—	—	10.13	13.00	—	—	—	—	80.44	482.64	424.47	58.17
M	—	—	—	—	—	2.06	—	3.50	—	2.81	—	2.94	2.06	—	—	3.12	16.49	98.94	375.31	-276.37
N	7.69	6.94	—	8.75	—	—	—	—	—	5.19	—	—	9.32	—	5.25	—	43.14	258.84	397.75	-138.91
O	—	4.93	—	—	—	5.62	6.44	—	—	—	4.88	—	—	—	5.50	6.50	33.87	203.22	362.35	-159.13
P	—	—	—	4.88	3.68	—	—	—	—	—	—	6.88	—	7.25	5.56	5.75	34.00	204.00	389.44	-185.44
Block Totals	89.81	67.18	76.74	70.07	71.06	56.80	68.01	78.44	82.99	53.94	55.19	62.95	62.38	70.19	54.37	60.80				

TREATMENTS

Treatment A Blue Wt. = 375 g.	Treatment B Blue Wt. = 373 g.	Treatment C Blue Wt. = 380 g.	Treatment D Blue Wt. = 379 g.	Treatment E Blue Wt. = 368 g.	Treatment F Blue Wt. = 363 g.
Drum 10 Minutes in: 3%N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 120 min. pH = 4.7 Drain Wash 5 min.	Drum 10 Minutes in: 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 120 min. pH = 4.8 Let stand in liquor over-night. pH of wash water = 3.8 Drain Wash 5 min.	Drum 10 Minutes in: 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.8 Add: 1% Sulfuric Acid 10% water Drum 30 min. pH = 2.6 Drain Wash 5 min.	Drum 10 Minutes in: 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.8 Add: 1% Sulfuric Acid 10% water Drum 30 min. pH = 2.5 Let stand in liquor over-night. Drain Wash 5 min.	Drum 10 Minutes in: 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.7 Add: 1% Sulfuric Acid 10% water Drum 30 min. pH = 2.5 Wash 30 min. Drain	Drum 10 Minutes in: 3% A. N. S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 120 min. pH = 4.0 Drain Wash 5 min.

Treatment G Blue Wt. = 363 g.	Treatment H Blue Wt. = 371 g.	Treatment I Blue Wt. = 377 g.	Treatment J Blue Wt. = 378 g.	Treatment K Blue Wt. = 379 g.	Treatment L Blue Wt. = 368 g.
Drum 10 minutes in 3% N.N.S. 25% H_2O Add: 5% M.M.R. 50% H_2O Drum 90 min. pH = 4.8 Add: 3% A.N.S. 25% H_2O Drum 30 min. pH = 3.7 Drain Wash 5 min.	Drum 10 minutes in 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.7 Add: 1% Acetic Acid 10% H_2O Drum 30 min. pH = 4.0 Drain Wash 5 min.	Drum 10 minutes in 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.7 Add: 1% Formic Acid 10% H_2O Drum 30 min. pH = 3.3 Drain Wash 5 min.	Drum 10 minutes in 3% N.N.S. 25% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.7 Add: 3% A.N.S. 25% H_2O Drum 30 min. pH = 3.6 Let stand in liquor over-night pH = 4.0 Drain Wash 5 min.	Drum 10 minutes in 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.8 Add: 1% Acetic Acid 10% H_2O Drum 30 min. pH = 4.0 Let stand in liquor over-night. pH = 3.7. Drain Wash 5 min.	Drum 10 minutes in 3% N.N.S. 50% H_2O Add: 3% M.M.R. 50% H_2O Drum 90 min. pH = 4.8 Add: 1% Formic Acid 10% H_2O Drum 30 min. pH = 3.3 Let stand in liquor over-night. pH = 3.3. Drain Wash 5 min.

Treatment M Blue Wt. = 386 g.	Treatment N Blue Wt. = 381 g.	Treatment O Blue Wt. = 386 g.	Treatment P Blue Wt. = 388 g.
Drum 120 min. in:	Drum 120 min. in:	Drum 120 min. in:	Drum 120 min. in:
100% H_2O	3% M.M.R.	3% N.N.S.	3% A.N.S.
pH = 3.3	100% H_2O	100 % H_2O	100% H_2O
Drain	pH = 4.2	pH = 3.7	pH = 2.7
	(N.B.Liquor was milky white in appearance after the run)	Drain	Drain
	Drain	Wash 5 in.	Wash 5 min.
	Wash 5 min.		

TABLE III

Analysis of Variance

Source of Variation	S.S.	D. F.	M.S.	M.S./M.S. Error	(P)
Rows	49.9976	5	9.99	10.3	0.001
Blocks*	280.6109	15	18.71	19.3	0.001
Treatments	1176.5439	15	78.44	80.9	0.001
Error	58.1542	60	0.969	——	
Total	1565.3066	95			

*Ignoring treatments.

TABLE IV

V Values and Corrected Means

Treatments	V Values	Corrected Treatment Means	Uncorrected Treatment Means
A	2.08	13.34	13.97
B	3.85	15.11	15.19
C	2.80	14.06	13.88
D	3.22	14.48	13.59
E	-0.11	11.15	10.92
F	-0.31	10.95	11.28
G	2.17	13.43	12.93
H	0.73	11.99	12.17
I	1.08	12.34	12.00
J	3.94	15.20	15.33
K	2.48	13.74	14.25
L	1.82	13.08	13.41
M	-8.64	2.62	2.75
N	-4.34	6.92	7.19
O	-4.97	6.29	5.65
P	-5.80	5.46	5.67

Statistical Analysis

An analysis of Variance, Table III, was conducted using the following statistical procedure as outlined in Brownlee [1], pages 147-149 from the data recorded in Figure 1 and that shown in items I through XIV.

I. Square each difference as sum, $\epsilon(n)^2$

II. Sum the differences and square, $(\epsilon n)^2$; divide by 96.

III. Sum the block totals, square each sum and add, $\epsilon(\text{block})^2$; divide by 6.

IV. Sum the rows, square each total and add, $\epsilon(\text{rows})^2$; divide by 16.

V. Arrange the treatments in the form of symmetrical incomplete blocks, see Table II. Sum each treatment and multiply by 6.

VI. Sum the block totals in which are contained the treatments to be studied, e. g., sum all blocks containing Treatment A, sum all blocks containing Treatment B, etc.

VII. Obtain Q values, i. e., V. minus VI. above, for each treatment, see Table II. (Q is the mean of each treatment minus the mean of the block totals in which that treatment occurs, multiplied by the number of units in a block.

VIII. Square each Q value and sum, $(Q)^2$

IX. a. I minus II = total Sums of Squares (Total S.S.) = A.

b. III. minus II = Sums of Squares of blocks, ignoring treatment effects = B

c. IV minus II = Sums of Squares of rows or replications = C

d. Sums of Squares of corrected treatment means =

$$(Q)^2 \times \frac{t - 1}{NK(K-1)} = D$$

t = No. of treatments, i. e., 16
N = Total No. of units, i. e., 96
K = No. of units per block, i. e., 6

e. Error Sums of Squares = A minus (B+C+D).

X. Divide S.S. of rows by 5 = Mean Square of rows, where 5 equals the number of degrees of freedom (D.F.).

XI. Divide S.S. of blocks and S.S. of treatments by 15 (D.F.), equals M.S. blocks and M.S. treatments.

XII. Divide S.S. error by 60 equals M.S. error. (Total D.F. = N-1 or 95. Error D.F. = 95 -(5 + 15 = 15) = 60

XIII. Divide M.S. values in XII and XIII by M.S. error (XIV).

XIV. Refer to "Tables of Variance Ratios" [1] to determine whether or not the mean square ratios in XV are significant at a probability level of 0.05. The values obtained in XV must be greater than that indicated in the tables in order to be significant.

XV. Obtain V. Values, deviation of treatment means from the grand mean corrected for block differences, where

$$V = Q \frac{(t - 1)}{N(K - 1)}$$

for each treatment. See Table IV.

XVI. Obtain corrected treatment means = V value plus grand mean, where grand mean = n divided by 96.

XVII. If significance exists, calculate L.S.D. term, i. e., Least Significant Difference, according to Yates as described in Brownlee [1], under Balanced Incomplete Blocks, where

$$\text{L.S.D.} = \pm\sqrt{2} \times \sqrt{\frac{K(t - 1)}{N(K - 1)}} \times \text{M.S. error} \times 2.0 +$$

$^{+}2.0$ = the value for "t", Table of $t^{(1)}$, at a probability level $^{(P)}$ of 0.05 for 60 D.F.

XVIII. Rank the corrected treatment means obtained in XI and categorize the means into levels according to their significant difference.

The analysis of Variance indicates a very high degree of significance of the effects of rows, blocks, and treatments, at probability levels of greater than 0.001. The Least Significant Difference term, between two means, was calculated using the formula shown previously and was found to be 1.20 (P=0.05). The application of the L.S.D. term will be shown later.

The problem of classifying an array of means into groups which are significantly different does not appear to have been completely solved by statisticians. Recently Tukey [5] has proposed a procedure for determining whether or not treatments within a major group or groups separated by the L.S.D. term differ from each other.

In order to classify the treatments means they are first arranged in order of magnitude, greatest to least. The L.S.D. term is applied to each of two adjacent values at a time. This operation is based on the principle that the L.S.D. term is merely an expression of a difference which would have been significant if there were only two varieties. A major group boundary exists when any gap between two adjacent treatments is greater than the L.S.D. term.

Categorization of our data in the above manner resulted in the separation of three major groups, the first group, "a", consisting of twelve mean values. All treatments containing combinations of syntan and methylol melamine are in this group. That they are more effective with regard to plumping when used together can readily be seen from the data shown in Table V. A further breakdown and classification of the means of Groug "a" into subgroups was effected by use of the Tukey Test for determining the "approximate unit normal deviate" from the following formula:

$$\frac{\frac{m - \bar{m}}{{}^{s}m} - 6/5 \log_{10} k}{3\,(1/4 + 1/n)} \quad (k > 3 \text{ means})$$

or

$$\frac{\frac{m - \bar{m}}{{}^{s}m} - 1/2}{3\,(1/4 + 1/n)} \quad (3 \text{ means})$$

$\bar{m}$ = the grand mean of the group

m = the worst straggling mean

${}^{s}m$ = Standard deviation of the mean of in this case $\sqrt{\frac{\text{Error mean square}}{6}}$

k = number of means in a group (must be greater than 3)

n = number of degrees of freedom used in obtaining the error mean square.

TABLE V

Classification of Corrected Mean Values for the Wet Leathers into Major Groups and Subgroups

Treatment	Corrected Mean Value	Group Designation	Brief Description of Treatment
J	15.20	a_1	Acidified with A.N.S. and aged overnight
B	15.11	a_1	No acidification with overnight aging.
D	14.48	a_2	Acidified with sulfuric acid and aged overnight.
C	14.06	a_2	Same as D with no overnight aging.
K	13.74	a_2	Acidified with acetic acid and aged overnight.
G	13.43	a_2	Acidified with A.N.S. with no overnight aging.
A	13.34	a_2	No acidification and no overnight aging
L	13.08	a_2	Acidified with formic acid and aged overnight.
I	12.34	a_3	Same as L, with no overnight aging.
H	11.99	a_3	Same as K, with no overnight aging.
E	11.15	a_3	Acidified with sulfuric acid and washed 30 minutes.
F	10.95	a_3	Same as A, but pretreated with an acid syntan.
N	6.92	b	M.M.R. alone, with no syntan pretreatment.
O	6.29	b	N.N.S. alone.
P	5.46	b	A.N.S. alone.
M	2.62	c	Blank

If the value obtained on solving the formula is greater than 1.96 (see Table of t, t=0.05, D.F.+), then at a probability of 5 in 100; the most

straggling mean does not belong in the major group. This process is repeated on the remaining values until no more stragglers can be separated from either side of the original set of figures. Means which are thus separated from one side are grouped and designated as a sub-group. Therefore it can be shown that (1) members within a group (either major or sub-group) do not differ significantly among themselves; (2) yet do differ significantly from members of other groups.

The classification of the sixteen corrected treatment means using the L.S.D. term and the Tukey Test, at P=0.05, is recorded in Table V. The data show that the major group classification "a" has been broken down into three sub-groups by the Tukey Test. These results indicate that the various combinations of syntan and methylol melamine together with modifiers can be separated into different degrees of effectiveness.

Discussion of Results

From the data presented it can readily be observed that the use of an acid or neutral syntan employed in conjunction with a methylol melamine resin increases the fullness of chrome tanned leather over that produced by any one of these agents alone.

The fullest leather is produced by aging in the syntan resin liquor overnight. The use of organic acids as acidifying agents appears to be detrimental to filling.

Prolonged washing of the leathers after resin application has a significantly deleterious effect upon plumpness. This is in all probability due to removal of the melamine resin in the wash water.

Leathers pretreated with an acid syntan showed poorer fullness than those pretreated with a neutral syntan. These results may be dependent upon the amount of active ingredient present in the syntan or may be related to the formation of synthetic tannin-chrome complexes.

It was observed that the melamine resin polymerized almost spontaneously when no syntans were present in the retanning liquor.

From the data presented the most desirable method of applying the syntan-resin retannage on a larger scale is that shown for Treatment A employing a neutral naphthalene syntan. This is based on the amount and cost of the materials used, the length of time of treatment and the degrees of plumping obtained. The necessity of overnight aging of the leathers in order to provide additional fullness is contingent upon the economics with regard to processing.

Summary

1. Employing a Youden Square design a series of sixteen retannages were conducted on chrome tanned side leather with neutral and acid naphthalene syntans in conjunction with a methylol melamine resin in order to arrive at a decision as to those treatments and procedures which most effectively increase plumpness.

2. A statistical comparison of the data obtained was made with the aid of the Analysis of Variance and the Tukey Classification Test, observing the plumping characteristics as influenced by the following factors:

a. Overnight aging of the leathers in the syntan-resin liquor.
b. The type of acidifying agent used: sulfuric acid, acid syntan and organic acids.
c. Prolonged washing of the leathers after the resin application.
d. Pretreatment of the leathers with neutral and acid syntans prior to resin application.
e. The application of the resin without a naphthalene syntan present.

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Received August 18, 1951

Discussion

R. M. Lollar: This paper represents a fine example of how the use of the proper experimental statistical procedures permits one to make valid decisions upon complicated treatment of facts, which otherwise would be difficult or impossible to make, at least without considerable additional work.

Dr. Turley should certainly be pleased to note how his prediction of the increase of the use of statistical design would occur has come true since it has been shown to us in the same afternoon.

Of course, in any one of the uses of mathematical procedures, we always ask the question, how well the results had been shown to correlate with later practical experience.

I noted in looking over the fifth table that these major groups did seem to have a pattern which was logical and which tends to give a confirmation to the accuracy of statistical procedures. But the proof of the pudding is in the eating, and that is, "Can you apply the results of these experiments into practice?"

I wonder, through some of their customer service work, whether the American Cyanmid has been able to see whether these conclusions are confirmed in practical scale work in the tannery.

F. D. Thayer: Yes, I would like to say that some of the work that has been shown in this report has been confirmed on a practical scale, and also other work that we have carried on in the laboratory employing statistical

procedures for evaluation, has been confirmed on a practical basis or has confirmed observations made in the tannery. That is, the work was carried on, and we confirmed that by statistical work. It works either way.

LOLLAR: I am particularly pleased to see this verification of applicability of statistical procedures to the leather industry, perhaps because it fits in with my own ideas, as you will see in the paper I will present on the question of an analysis of retan leather.

THAYER: There is one thing I would like to say before concluding, and that is that statistics lead you to the making of a decision. It is not going to solve all your problems or tell you why things are so or why they are not so. You cannot expect statistics to do everything.

ABSTRACTS

The Behavior and Evaluation of Tannin Fixing Agents. By Erich Böhme and L. K. Schwörzer. *Das Leder*, **2**, 97 (1951). In making factory type sole leather by the new, rapid tanning method, the leather is treated with a material to fix the uncombined tannin. At present the demand is for a flexible, natural colored leather of not too high specific gravity, with low water solubles and with low water absorption. Such leather may be obtained also by impregnation, as little, if any, distinction can be made between impregnation and fixation of uncombined tannin. Fixing agents in use consist of sizing materials of all kinds, degraded glue, casein, either alone or mixed with oils, soaps, Epsom salt, or sugars. After the fixing agent, treatment with formaldehyde occasionally follows. The agent should not only irreversibly fix the excess tannin, but should also equalize and lighten the color and reduce water absorption. Commercial agents fill these requirements very well.

Hexamethylenetetramine and derived products fix the tannin not only on the surface, but throughout the leather; however, auxiliary tannins that lower the pH value below 3.5 must not be used or formaldehyde and ammonia will be liberated. High molecular condensation products mainly fix surface tannin. Rather small amounts of fixing agent give best results; too much may reverse its action and result in increased water solubles. For evaluating an agent, a solution of known tannin content may be treated with increasing amounts of the fixing agent, after which the precipitate that forms may be filtered and weighed. From these data one can determine the suitability of the agent, the proper amount to use and the expected effect on color and other properties of the leather. The method is as follows: Prepare the tannin solution in the usual manner, filter through a filter candle and adjust the pH to 3.5–4.5. The solution must not be too concentrated or the precipitate will be difficult to filter, nor too dilute or a precipitate will be slow to form. In general, prepare a 10 per cent solution of a solid extract, or a solution between 2° Be and 6° Be. Prepare a 10 per cent or 20 per cent aqueous solution of the fixing agent and filter. To 100 cc. portions of the tannin solution at room temperature add suitable increasing amounts of the fixing solution (for example 10, 20, 30 cc.). Cover the vessels and leave for 24 or 48 hours in the dark. Filter through 25-50 cc. Jena glass filters, using gentle suction. Note appearance and color of the precipitate at the start and end of filtration. Wash with 25 cc. of water, suck dry, then dry below 50°C to constant weight. If the filtrate is cloudy use a finer filter, or if this is not effective, stir a weighed amount of a filter aid such as Kaolin into the solution before filtering. I. D. C.

The Structure of Fibrous Proteins of the Collagen-Gelatin Group. By L. Pauling and R. B. Corey. *Proc. Nat. Acad. Sci.* **37**, No. 5, 272 (1951). The diffraction pattern of collagen and gelatin is characterized by a meridional arc at 2.86 A. This arc is essentially uninfluenced by a change in source of material or in previous treatment. The principal equatorial reflection, which for dried tendon corresponds to the spacing 10.4 A, varies greatly in spacing with source and treatment of material. Collagen evidently consists of polypeptide chains extending along the fiber axis and rather loosely packed in parallel orientation. As explained below, the equatorial reflections correspond to a hexagonal packing of circular cylinders.

On the basis of the configuration of the amide group in a peptide, as predicted from X-ray investigations by the authors on related simple substances, the length of an amide group with the cis configuration is 2.83 A, which is close to the observed fiber-axis spacing. A structure is formulated with use of polypeptide chains in which there is an alternation of two cis groups and one trans group as shown in Figure 1.

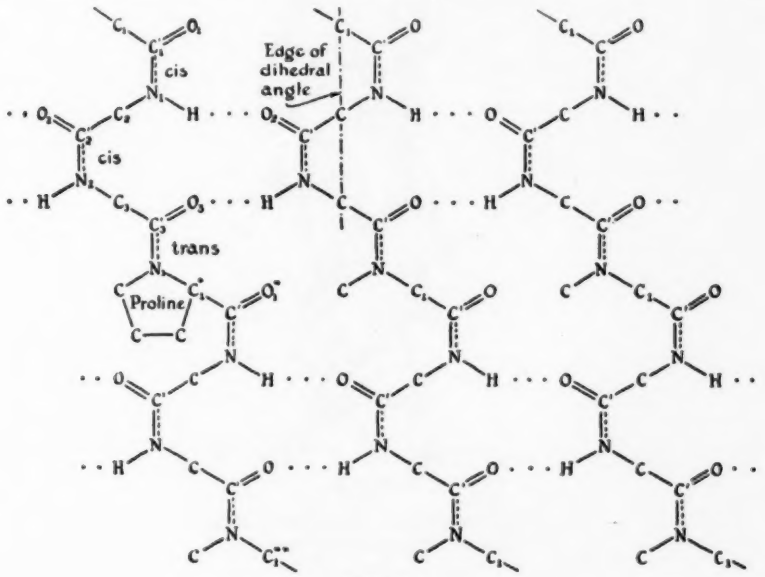


FIGURE 1

Diagrammatic representation of the configuration of polypeptide chains in the collagen-gelatin three-chain helix.

The ease of lateral swelling of collagen indicates lack of hydrogen bonding between molecules but the presence of intramolecular hydrogen bonding. For cylindrical molecules in hexagonal packing the principal equatorial spacing of 10.4 A (for dried collagen) recalculated for $d_{10.0}$ leads to 125 A^2 as the basal-plane area per molecule, and with 2.86 A as the fiber axis length to 358 A^3 as the volume per unit, or 215 cm^3 per mole of units. The mass per unit is 291 g, and since the average residue weight for collagen and gelatin is found by

analysis to be slightly less than 100, there are about three residues in the unit of the molecule (2.86 A length). It is concluded, therefore, that the collagen or gelatin molecule consists of three polypeptide chains. The intramolecular hydrogen bonds in the collagen-gelatin molecule must be lateral bonds between the three polypeptide chains that constitute the molecule.

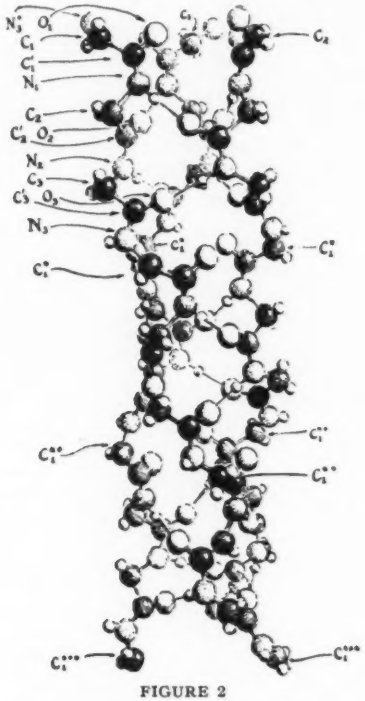


FIGURE 2

Drawing representing the proposed structure of the collagen-gelatin molecule.

A structure is postulated in which each of the three polypeptide chains is coiled into a helix, the coiling being achieved through the bending of the chain at the position of the α carbon atoms, and the three helixes having a common axis. For the ideal configuration, in which the three α carbon atoms are similarly oriented directly above and below one another along a line parallel to the fiber axis, the dihedral angle at these carbon atoms is 97° C. Some distortion of the structure is required in order that satisfactory hydrogen bonds be formed. This distortion consists in a rotation around the two single bonds formed by the α carbon atoms, so as to draw the α carbon atom C_3 (see Figure 2) closer to the axis of the helix by 0.34 A than the α carbon atoms C_1 and C_2. The hydrogen bonds are introduced in such a way that the three chains of the molecule are related to one another by a three-fold

axis of symmetry. The α carbon atoms C_α lie at the corners of an equilateral triangle of edge 5.60 A, and the atoms C_1 and C_3 at the corners of an equilateral triangle with edge 6.20 A. The two cis amide residues are rotated by about 9° out of the orientation parallel with the fiber axis. The trans residue is rotated through 30° about its $C_3 \ldots C_1$ axis. The trace of this axis on the basal plane is 2.44 A. The relation of this trace to the 6.20 A triangle of the C_3 and C_1 atoms is such that the angle of rotation about the fiber axis that converts one three-residue element of a polypeptide chain into the element following it in the chain is 40°. This angle of rotation can hardly be varied by more than 3° without introducing unsatisfactory structural features. The helix formed by a single chain of the collagen molecule is thus found to have very nearly a nine-fold screw axis of symmetry.

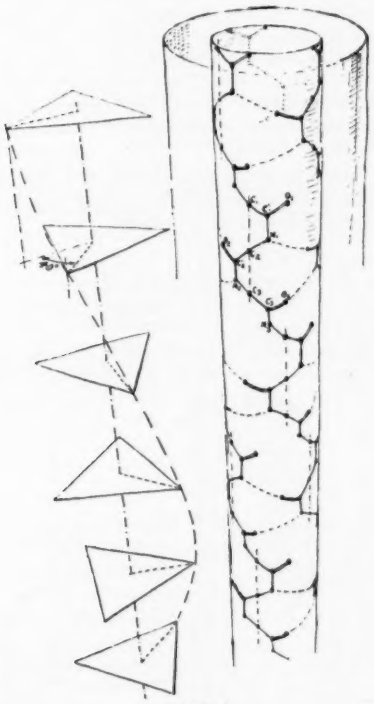


FIGURE 5

Diagrammatic representation of the collagen three-chain helix.

The translation of the operation converting one structural element into the following one in the chain is given for the proposed model as 8.58 A, which corresponds to 2.86 A per residue, in exact agreement with the X-ray value.

The nature of the inter-chain interactions is shown in Figure 1. Two hydrogen bonds are formed per unit. The $N_1 - H \ldots O_2$ bond has a length of 2.63 A. The $N_2 - H \ldots O_3$ hydrogen bond has the length 2.83 A. If the model were to be changed by a small additional rotation of the trans amide group the distance would be significantly shortened.

The correlation between the chemical composition of the collagen-gelatin proteins and the existence in the structure of the two rather than three hydrogen bonds per element is pointed out. Chemical analysis shows one-third of the amino acids in collagen and gelatin are proline or hydroxyproline. In residues of these amino acids the nitrogen atom does not have an attached hydrogen atom and so does not enter into hydrogen-bond formation.

The structure of the collagen-gelatin molecule can be represented diagrammatically as shown in Figure 5. The three helical polypeptide chains are shown projected onto the surface of a cylinder. This structure of the molecule provides immediate explanation of the principal mechanical property of collagen, its extensibility over only a limited range. The effective fiber-axis length of the trans residue in the molecule as shown is 2.93 A. If on the application of force this residue were to be twisted into a parallel orientation, its effective length would be 3.83 A, the C_α–C_1 distance. This maximum increase in length corresponds to a 10 percent extension of the molecule. It is likely, however, that the bond angles and planarity of amide groups would prevent complete parallel orientation, and that only a somewhat smaller extension could be achieved.

The way in which the molecules are packed together in a fiber of tendon is shown in Figure 6. The cylindrical molecules are arranged in hexagonal packing. They are all helical with the same sense, either right-handed or left-handed.

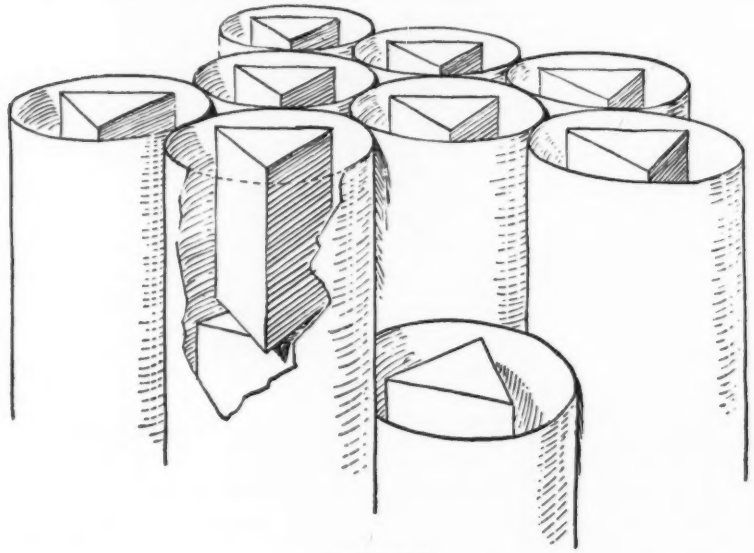


FIGURE 6

Diagrammatic representation of an aggregate of collagen molecules in a collagen fiber.

The proposed structure accounts in a striking way for the principal features of the X-ray diffraction pattern of collagen and gelatin. A fiber consisting of these cylindrical molecules in hexagonal packing, with $a_0 = 12.50$ A (at normal humidity), would be predicted to produce equatorial reflections (10.0), with d = 10.83 A, (11.0), with d = 6.25 A, (20.0), with d = 5.42 A, and (22.0), with d = 3.13 A. Published data show strong reflection at 10.9 and a medium reflection at 5.42 A. Calculation of the form factor for collagen on the assumption of cylindrical symmetry leads to the prediction that a minimum in intensities of reflections would occur at about d = 7.14 A and another minimum at d = 2.89 A. These values are close to those of 6.25 A and 3.13 A mentioned above.

The predicted unit of structure of crystalline collagen, except for perturbations due to the distribution of side chains is a hexagonal unit with $a_0 = 12.5$ A (normal humidity) and $c_0 = 25.74$ A, the fiber axis distance for nine residues. J. M. C.

Alcohol Fractionation of Swedish Pine Bark Extract. By A. Haglund. *Oesterr. Leder-Zeitung*, **5**, 404, (1950). Swedish pine bark contains 16-19 percent tannin (filter method) and has a purity of 65-68. Extract made from the bark has a purity of 60-65, a tanning value of 83-91 and a combining value of 55-61, but it contains much sediment and makes dark brown, hard, empty leather. Extract containing 36-38 percent dry matter was separated into two fractions by addition of benzene-denatured alcohol to give a concentration of from 50 to 80 percent alcohol (on water-alcohol basis). The precipitate was filtered in a Büchner funnel, washed with 50-80 percent alcohol, then taken up in water. Alcohol was removed from each fraction by evaporation in vacuum. Fraction 1 (alcohol insoluble) was a brownish gray, viscous fluid, whereas fraction 2 was a clear mobile liquid. Alcohol fractionations were also made of tanning liquors after they had been used for tanning pieces of skin for 20, 66 and 134 hours. Only a relatively small amount of the alcohol insoluble fraction was taken up by either hide powder or pieces of skin. During tanning, the alcohol insoluble fraction in the liquor becomes greater but the amount absorbed by skin never becomes equal to the amount of alcohol soluble material taken up. I. D. C.

Contributions on Pine Bark Tannin. I. Separation of a Pine Bark Extract into Two Fractions by Partial Tannin Precipitation with Ethyl Alcohol. By A. Haglund. *Das Leder*, **2**, 145, (1951). Küntzel and Melzer [*J.A.L.C.A.* **43**, 613] first separated pine bark extract into fractions with ethyl alcohol and found that the fractions differed in tanning value. The present work on Swedish pine bark was undertaken in the hope that a method for improving the extract might be found. The material was a technical, liquid, pine bark extract made with mild sulfiting; it contained all of the tannin from the bark including that which is difficult to extract. To the liquid extract, having a tannin content of 21-23 percent, alcohol was added until the alcohol concentration was 80 percent. The precipitate (fraction 1) was dissolved in water then concentrated as far as possible under vacuum to remove alcohol. The solution (fraction 2) was not evaporated to dryness but only to the concentration of a liquid extract.

Fraction 1 foamed excessively and could not be concentrated to more than 25 percent because of its high viscosity. It had a high insolubles content which did not settle because of the viscosity. Fraction 2 was fluid when concentrated to 60 percent dry matter and remained clear on dilution. The following analytical data were obtained:

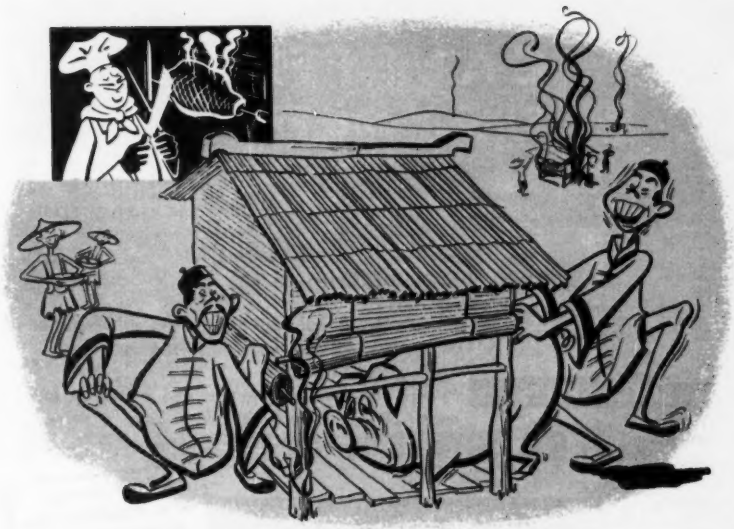
	Original extract	Fraction 1	Fraction 2
Dry matter, % of original extract	100	32.7	67.3
Tannin, %	58.4	37.2	59.4
Nontannin, %	37.3	42.6	39.1
Ash (on dry matter), %	2.8	4.8	1.8
Tanning value	84.1	68.5	102.6
Combining value	51.2	56.1	60.8
Purity by filter method	61	62	60
Purity by shake method	45	22	43
Difference in purity (astringency)	16	40	17
Insolubles, %	4.3	20.2	1.5
Salted out at 1/3 saturated, %	21.4	—	14.4
Salted out at 2/3 saturated, %	16.2	—	17.0
Salted out at 3/3 saturated, %	16.4	—	13.3
Not salted out, %	41.3	79.8	48.2

Fraction 1 appeared to be more stable than fraction 2 because it was not salted out, however this lack of precipitation by salt may be due to the high viscosity. Fraction 1 made hard, dark, worthless leather similar to that made from pure lignin extract. Fraction 2 produced a soft, light leather suitable for fine leather work; this leather was better than that made with the unfractionated extract. Removal of Fraction 1 would improve pine extract. Fraction 1 consists principally of neutral salts. Its high viscosity and other characteristics indicate that the the acids present as neutral salts are quite different from the acids found in Fraction 2. I. D. C.

A Method for Determining the Amount of a Tanning Extract that can be Salted Out. By A. Haglund. *Das Leder*, **2**, 150 (1951). The method for determination of insolubles in tanning extracts [published in *J.A.L.C.A.* **44**, 68, (1949)] has been applied to the determination of the fraction of an extract salted out at various salt concentrations. The method is as follows: To a weighed, 50 ml. centrifuge tube add from 20 to 40 grams of a 1 percent tanning solution and reweigh (A). Add salt in the required amount to make the solution 1/3, 2/3, or 3/3 saturated with salt. Stopper the tube, shake by machine for 15 minutes, then centrifuge 90 minutes at 3000 revolutions. Pour off the supernatant liquid and weigh the wet tube containing the precipitate (B). Wash the tube contents into a porcelain dish, evaporate, dry, and weigh (C). Ash the residue, determine chloride by titration, calculate as sodium chloride and subtract this weight from the weights B and C. The true weight of material salted out (X) can then be found from the equation $(B\text{-}X)b/100 + X = C$ where b is the concentration of the centrifuged solution. b can be determined directly by evaporating some of the clear solution or can be calculated from the equation: $b = 100[(Aa/100)\text{-}C]/(A\text{-}B)$ where a is total solids in the original solution. I. D. C.

The Use of Statistical Research in the Leather Industry. By J. A. Sagoschen and K. F. Martin. *Oesterr. Leder-Zeitung*, **5**, 390, (1950). A discussion of the value of statistical methods in the control of leather quality. I. D. C.

Corrosion Protection in the Leather Industry with Special Consideration of Chlorinated Rubber Coatings. R. Leukauf. *Oesterr. Leder-Zeitung*, **5**, 408, (1950). A lecture. I. D. C.



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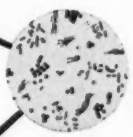

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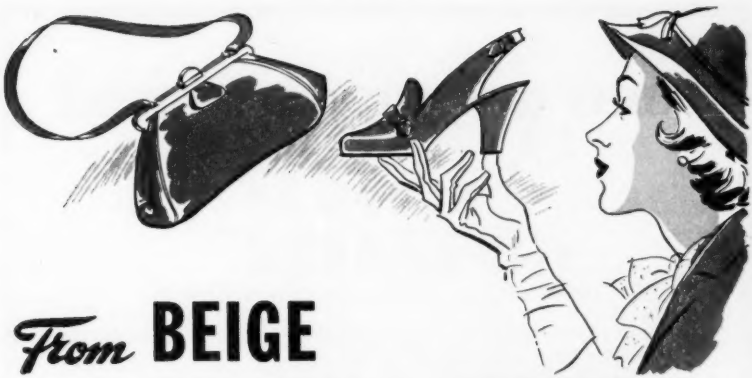

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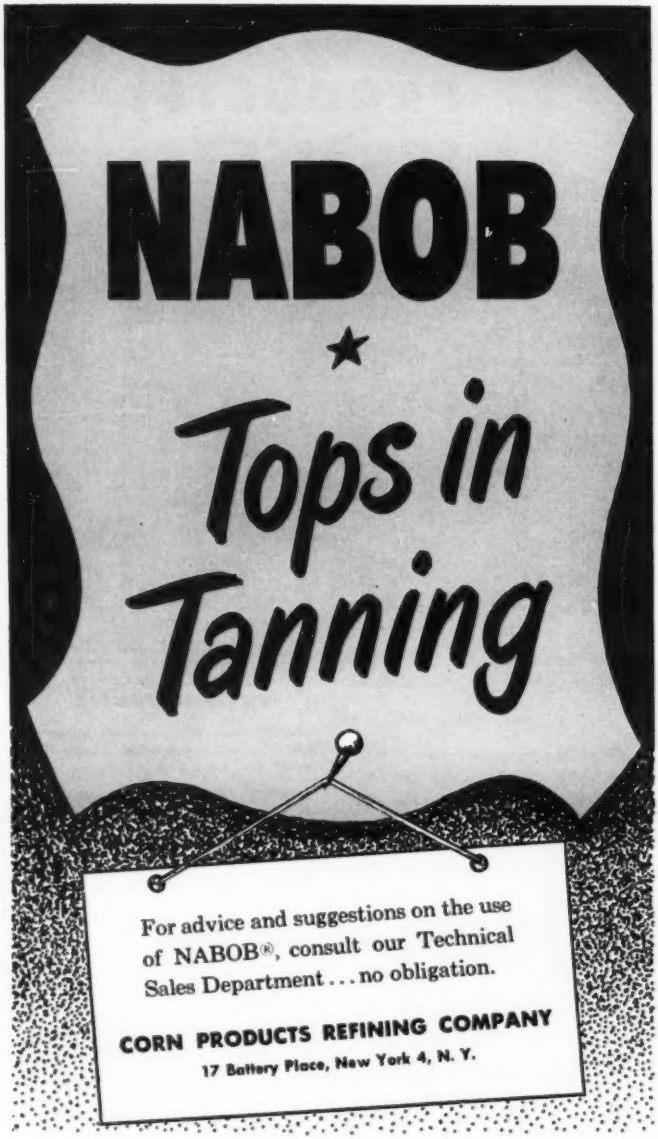
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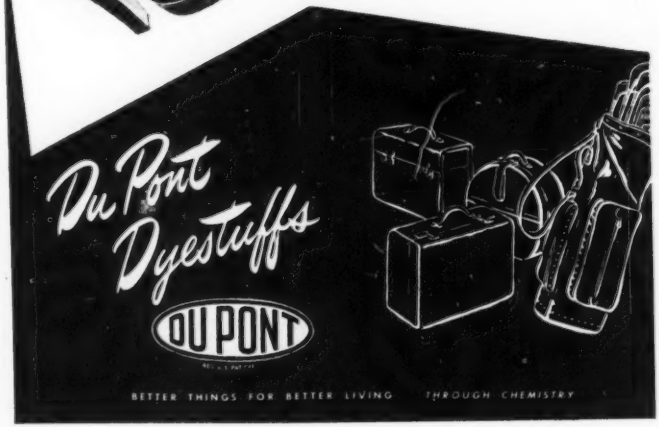

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